

# PATENT SPECIFICATION

(11)

1329 049

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NO DRAWINGS

- (21) Application No. 41475/71 (22) Filed 6 Sept. 1971  
 (31) Convention Application No. 72555 (32) Filed 15 Sept. 1970 in  
 (33) United States of America (US)  
 (44) Complete Specification published 5 Sept. 1973  
 (51) International Classification C08F 29/16  
 (52) Index at acceptance

C3P 10C13A 10C13B 10C13C 10C14A 10D4A 10D5  
 10K10 10K6 6C13A 6C13C 6C14A 6D3 6K10



## (45) COATING COMPOSITIONS

(71) We, E. I. DU PONT DE NEMOURS & COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to tetrafluoroethylene polymer aqueous dispersions used for coating purposes, and more particularly to such dispersions which provide coatings of improved gloss.

The properties of non-melt-fabricable tetrafluoroethylene polymers such as high temperature resistance, chemical stability, and low friction surface, have led to the widespread use of these polymers in the form of films, coatings and impregnants. Unfortunately, the nature of the polymer, i.e. the fact that it is sintered rather than melt-fabricated, causes the exposed surface of the polymer to have some degree of roughness which, in turn, renders the surface not as glossy as desired for some applications for aesthetic or for functional reasons.

It has now been found that the gloss of coatings obtained from aqueous dispersions of a non-melt-fabricable tetrafluoroethylene copolymer can be improved by incorporating into the dispersion a small, gloss improving, amount of a dispersion of a melt-fabricable tetrafluoroethylene copolymer and a nonionic surfactant. Accordingly the present invention provide a coating composition which comprises an aqueous dispersion of:

- (a) a non-melt-fabricable (as hereinafter defined) tetrafluoroethylene polymer, (b) 1 to 6% by weight, based on the weight of (a), of a melt-fabricable (as hereinafter defined) tetrafluoroethylene copolymer, and containing, dissolved therein, a non-ionic surfactant.

The resultant aqueous dispersion when cast in a conventional manner such as by contacting a substrate and the dispersion, followed by drying the dispersion and sintering the tetrafluoroethylene polymer (a), yields a tetrafluoroethylene polymer coating of improved gloss over that which is obtained for the current commercially available tetrafluoroethylene polymer dispersions.

Each component of compositions of the present invention, i.e. the non-melt-fabricable tetrafluoroethylene polymer (a) (as aqueous dispersion), the melt-fabricable tetrafluoroethylene copolymers (b) (as aqueous dispersion), and the surfactant, is a well-known material of commerce. More specifically, the non-melt fabricable tetrafluoroethylene polymer component can be obtained as a dispersion of colloidal particles of non-melt-fabricable tetrafluoroethylene polymer in water. Examples of such dispersions include those disclosed in U.S. Patent Specifications Nos. 2,534,058, (Renfrew), 2,559,752, (Berry), and 2,559,749, (Benning), as well as the concentrated tetrafluoroethylene polymer aqueous dispersions disclosed in U.S. Patent Specifications Nos. 2,478,229, (Berry) and 3,037,953 (Marks and Whipple), and the large particle dispersions disclosed in U.S. Patent Specification No. 3,391,099 (Punderson). The tetrafluoroethylene polymer in the aqueous dispersion can be a homopolymer or a copolymer of tetrafluoroethylene with a small amount of another copolymerizable monomer, such as up to two percent by weight of units derived from perfluoroalkyl ethylene or oxyperfluoroalkyl trifluoroethylene of 3 to 10 carbon atoms, as disclosed in U.S. Patent Specification No. 3,142,665, (Cardinal, Edens, and Van Dyk). The preferred comono-

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mer is hexafluoropropylene. The resultant tetrafluoroethylene polymer must retain its non-melt-fabricable character.

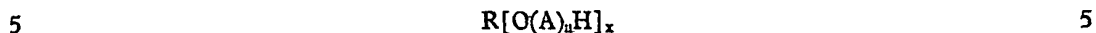
Briefly, a process for making the dispersion generally involves introducing tetrafluoroethylene under pressure into an aqueous solution of a polymerization initiator and a dispersing agent under mild agitation to produce an aqueous dispersion of colloidal size particles of tetrafluoroethylene polymer in concentrations of 15 to 45 percent by weight of polymer solids. The present invention does not depend on which polymerization initiator and dispersing agent are used so long as the product obtained is an aqueous dispersion of tetrafluoroethylene polymer. Typically, however, the initiator will be a water-soluble peroxy compound such as an inorganic persulfate, e.g. ammonium persulfate, or an organic peroxide, e.g. disuccinic acid peroxide, and the dispersing agent used during polymerization will be an anionic dispersing agent which imparts a negative charge to the polymer particles in the dispersion. The most used anionic dispersing agents are the fluorinated carboxylic acid or carboxylates, e.g. an ammonium polyfluorocarboxylate containing from 7 to 10 carbon atoms. The amount of dispersing agent usually used is from 0.2 to 0.8 percent based on the weight of polymer solids. The dispersion may be used in the present invention in this form or may be concentrated to higher solids contents such as up to 75 percent by weight polymer solids. Preferably, the particle size of the tetrafluoroethylene polymer particles in the dispersion are of the larger size variety, i.e. at least 0.3 micron in average particle diameter which can be made by the process of the aforementioned Punderson patent by gradually adding the dispersion agent to the polymerisation system during the early stage of polymerisation. The particles can be spherical or irregular in shape, for example elongated. Particle size is determined by the light scattering method disclosed in the Punderson patent, except that the refractive index increment is taken as 0.020 because of the presence of surfactant.

With respect to the melt-fabricable tetrafluoroethylene copolymer component of the composition of this invention, the polymer thereof is a copolymer of tetrafluoroethylene with at least sufficient other ethylenically unsaturated copolymerisable monomer to render the resultant polymer melt fabricable. "Melt fabricable" means that the copolymer has a specific melt viscosity of less than 10<sup>7</sup> poises at 380°C. at a shear stress of 6.5 psi; conversely, "non-melt-fabricable" means that the polymer has a specific melt viscosity of 10<sup>7</sup> poises or more at 380°C. at a shear stress of 6.5 psi. Any other monomer which has the effect of making the resulting copolymer melt-fabricable when copolymerised with tetrafluoroethylene can be used. Usually, no more than 35 percent by weight of the copolymer will be formed from such other monomer or monomers. Examples of such copolymers include the tetrafluoroethylene/hexafluoropropylene copolymers disclosed in U.S. Patent Specification No. 2,946,763 (Bro and Sandt), the copolymers of tetrafluoroethylene with higher perfluoroalkenes such as those containing from 4 to 10 carbon atoms, copolymers of tetrafluoroethylene with perfluoro(alkyl vinyl ethers), e.g., perfluoro(propyl or ethyl vinyl ethers) disclosed in U.S. Patent Specification No. 3,132,123 (Harris & McCane), and the copolymer of tetrafluoroethylene with perfluoro(2-methylene-4-methyl-1,3-dioxolane) disclosed in U.S. Patent Specification No. 3,308,107 (Selman and Squire), and the copolymers of tetrafluoroethylene with highly fluorinated monomers, i.e. in which a single hydrogen substituent remains which does not change the fluorocarbon character of the polymer, such monomers being 2-hydroperfluoroalkene containing 3 to 10 carbon atoms, e.g., 2-hydropentafluoropropene, the *omega*-hydroperfluoroalkenes from 3 to 10 carbon atoms, and the *omega*-hydroperfluoroalkyl perfluorovinyl ethers in which the alkyl group contains from 1 to 5 carbon atoms.

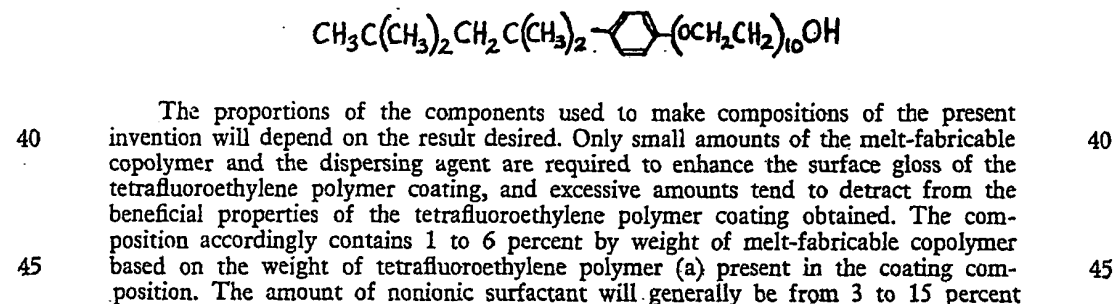
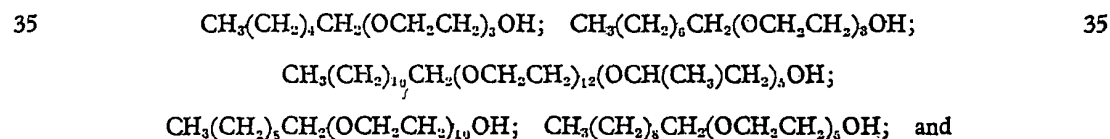
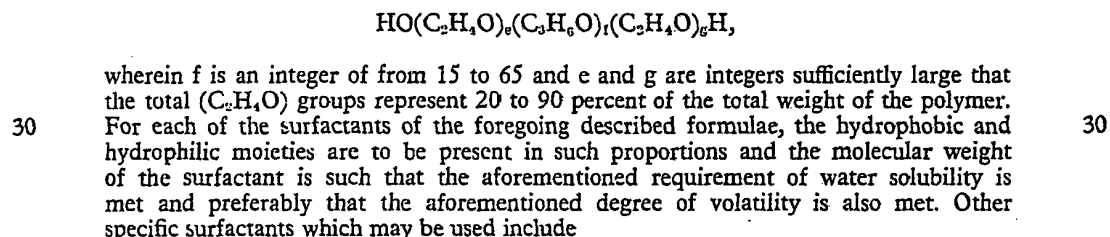
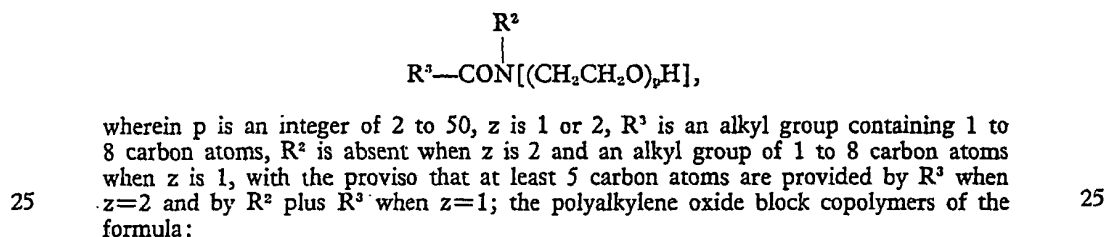
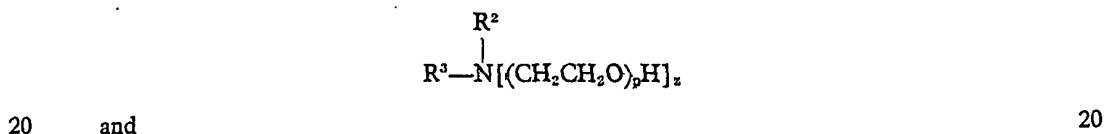
Aqueous dispersions of the above-described copolymers can be prepared substantially in the same way as the tetrafluoroethylene polymer aqueous dispersions referred to above. For example, the procedure of Example 1 of U.S. Patent Specification No. 2,946,763 (Bro and Sandt) can be followed.

The surfactant component of composition of the present invention is any nonionic surfactant which is soluble in water at room temperature (20–25°C.) at the concentration desired. The nonionic surfactant can be composed of a single surfactant or a mixture of nonionic surfactants. The nonionic surfactant preferably should have sufficient volatility so that at least 95 percent by weight of the surfactant is burned out of the tetrafluoroethylene polymer during its sintering which is generally done at a temperature in the range of 340 to 400°C. for 5 seconds to 10 minutes. Typically such surfactants are prepared as reaction products of ethylene oxide with such other compounds which impart hydrophobic moieties to the resultant surfactant, e.g. propylene oxide, amines, saturated and unsaturated alcohols and acids, and alkyl phenols. Other suitable nonionic surfactants which do not involve reaction with ethylene oxide

but which can be used in the present invention are the alkanol amides and fatty esters, such as the methyl esters of caprylic, caproic, stearic, and oleic acids. For purposes of illustration, some of the foregoing mentioned non-ionic surfactants are further illustrated hereinafter by the formulae:



wherein (A)<sub>n</sub> is the group  $-(C_2H_4O)_n-$  or a mixture of the groups  $-(C_2H_4O)_a-$  and  $-(C_3H_6O)_b-$ , wherein n in each instance is an integer of from 2 to 50 and preferably 2 to 18, b is 0 or an integer of up to 30, and a is an integer of at least 2, (a+b) is equal to n; x is 1, 2 or 3; and R is an aliphatic hydrocarbon group which can be saturated or unsaturated, straight-chain, branched, or cyclic, and will generally contain from 8 to 24 carbon atoms, preferably from 8 to 18 carbon atoms; examples of R groups include oleyl, stearyl, tridecyl, lauryl, decyl and the groups derived from aliphatic glycols and triols;  $R'-C_6H_4O(B)_mH$ , wherein (B)<sub>m</sub> is the group  $-(C_2H_4O)_m-$  or a mixture of the groups  $-(C_2H_4O)_c-$  and  $-(C_3H_6O)_d-$ , wherein m in each instance is an integer of from 2 to 50 and preferably 8 to 20, d is 0 or an integer of up to 30, c is an integer of at least 2, (c+d) is equal to m; R' is a monovalent aliphatic and usually saturated and containing 4 to 20 carbon atoms and preferably 8 to 12 carbon atoms; 10 15



based on the total weight of polymer solids (tetrafluoroethylene polymer (a) and copolymer (b)) present in the composition, with the preferred range being from 4 to 9 percent by weight. The proportion of polymer solids in the composition is preferably from 40 to 65 percent based on the total weight of the composition.

The compositions of the present invention can be prepared by blending separate aqueous dispersions of the tetrafluoroethylene polymer (a) and copolymer (b). The surfactant may be dissolved in either of the dispersions or in the resultant blend thereof. The blending step is generally done with mild agitation so as to avoid coagulation of the aqueous dispersions and/or the resultant blend thereof. Further details on blending dispersions of this type for the purpose of preparing colloidal blends of a tetrafluoroethylene polymer with a tetrafluoroethylene/hexafluoroethylene copolymer is disclosed in U.S. Patent Specification No. 3,051,683 (Mallouk).

The compositions of the present invention may be cast in a conventional manner by contacting a substrate and the composition, followed by drying and sintering of the tetrafluoroethylene polymer (a) to give a polymer coating of improved gloss. The contacting step can take the form of spraying the dispersion onto the substrate or dipping the substrate into the dispersion to coat and/or impregnate the substrate. If the substrate is smooth surfaced, the coating can be removed to form film. The coating (or film) thickness can be built-up by repeated coating after each drying and sintering cycle.

The following Examples illustrate the present invention; (parts and percents are by weight unless otherwise indicated):

**PREPARATION OF COMPOSITION** — The co-dispersions were prepared by blending an aqueous dispersion of polytetrafluoroethylene (polymer (a)) with an aqueous dispersion of copolymer (copolymer (b)) under mild agitation to avoid coagulation. The nonionic surfactant was added neat, or as an aqueous solution, to the dispersions. The polymer solids concentration in the resultant dispersion was 49 percent based on the total weight of the dispersion.

**MEASUREMENT OF GLOSS** — Glass fabric (#128 type) was coated with various dispersion formulations according to the procedure described below. A swatch of cloth,  $5\frac{1}{2}'' \times 5''$ , preferably coated with cement on all four edges to keep the cloth from unravelling, was clamped on opposite sides to a stretching apparatus. The apparatus was adjusted so that the cloth was taut. The stretched cloth was then dipped into the dispersion being tested for 15 seconds. After removal from the dispersion, the cloth was allowed to dry for 30 minutes at room temperature. This was followed by heating at  $100^{\circ}\text{C}$ . for 5 minutes and at  $380^{\circ}\text{C}$ . for four minutes. The cloth was flat and held its shape. Successive coats (either 5 or 6) were made in the same manner except the cloth was simply held by one  $2\frac{1}{2}''$  wide spring-loaded jaw clip. After the final coat, the coated cloth sample was trimmed to dimensions of about  $4 \times 4''$ . The gloss of the square  $4 \times 4''$  sample was measured using a Portable Gardner 60° Glossmeter, Model GC-9045 (P-5), according to the procedure described below. The instrument was standardised first. It was placed on the surface of a primary black gloss standard, which had been cleaned, in a manner such that the light exiting the aperture was focused directly on the centre of the plaque. The glossmeter was turned on and allowed to warm up for at least 30 minutes. The rheostat knob was then adjusted until the meter read 94%. In a similar manner, the glossmeter was adjusted to  $30 \pm 1\%$  using a secondary white standard. This calibration was checked occasionally during gloss reading determinations. The coated cloth sample was then placed on a  $4\frac{1}{2}'' \times 4\frac{1}{2}'' \times \frac{1}{2}''$  wooden plaque previously painted with flat black paint. After positioning the sample so that the edges were parallel with those of the plaque, the glossmeter was placed on the sample in such a manner that (1) the light exiting the aperture was focused directly on the centre of the sample and (2) the direction of the horizontal component of the light beam was parallel to an edge of the sample. At the end of a few seconds, the reading from the glossmeter was recorded. Two more readings were taken after the glossmeter had been moved successively to slightly different positions. Further series of three readings were obtained in the horizontal direction perpendicular to the above horizontal direction; similar series were taken on the other side of the coated glass cloth in the mutually perpendicular directions defined by the edges of the cloth. The overall average was taken as the gloss reading. Usually, the average of the readings in different directions was within  $\pm 1$  unit on the glossmeter scale.

#### EXAMPLE 1

In this Example, the tetrafluoroethylene polymer (a) aqueous dispersion contained 60 percent polytetrafluoroethylene solids based on the total weight of the dis-

persion, 6 percent of polyethylene glycol mono-para-octylphenyl ether, available as "Triton" X-100, based on the weight of polymer and had an average particle diameter of 0.23 micron. The coating of polytetrafluoroethylene on glass fabric, prepared by the previously described general procedure gave a glossmeter reading of 6 for seven coats having a total thickness of 9.7 microns.

A blend of this dispersion was prepared with 3 percent of "Triton" X-100 (based on the weight of the polytetrafluoroethylene in the dispersion) and 3 percent by volume based on the total volume of the co-dispersion of an aqueous dispersion of a tetrafluoroethylene/hexafluoropropylene copolymer containing 55 percent copolymer solids by weight, having an average particle diameter of 0.16 micron, and containing 6 percent "Triton" X-100 nonionic surfactant (based on the weight of the copolymer (b)) and having an infrared ratio of 3.49 ( $A_{10.18\mu}/A_{4.25\mu}$ ) as measured by the procedure disclosed in U.S. Patent Specification No. 2,946,763 (Bro and Sandt) and a specific melt viscosity of  $6-10 \times 10^4$  poises at  $380^\circ\text{C}$ . at a shear stress of 6.5 psi.

The total surfactant content was about 9 percent based on the total weight of polymer solids. Water was added to reduce the polymer solids content to 49 percent. The coating of the polymer blend for this co-dispersion on glass fabric, prepared by the previously described general procedure gave a glossmeter reading of 15 for seven coats having a total thickness of 9.4 microns.

This experiment was repeated except that the polytetrafluoroethylene in the polytetrafluoroethylene aqueous dispersion had a standard specific gravity (SSG) of 2.23 as compared to 2.22 for the polytetrafluoroethylene in the dispersion used earlier in this Example. The polytetrafluoroethylene aqueous dispersion by itself gave a glossmeter reading for the coating of 8 for seven coats having a total thickness of 9.5 microns. The composition consisting of this dispersion and the copolymer (b) dispersion (2 percent by volume) and surfactant gave a glossmeter reading for the coating of 20 for seven coats having a total thickness of 9.6 microns.

#### EXAMPLE 2

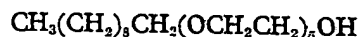
The procedure of Example 1 was repeated except that (a) the tetrafluoroethylene polymer (a) of the aqueous dispersion was replaced by a copolymer of tetrafluoroethylene and hexafluoropropylene as described in U.S. Patent Specification No. 3,142,665 (Cardinal, Edens, and Van Dyk) having an infrared ratio of 0.39 ( $A_{10.18\mu}/A_{10.7\mu}$ ) and an average particle diameter of 0.18 micron (using a refractive index increment of 0.020 gms/cc), and (b) the total concentration of "Triton" X-100 was 8 percent based on the weight of total polymer solids. The composition of the co-dispersion plus surfactant gave a glossmeter reading of 18 for the coating of seven coats having a total thickness of 9.2 microns. The aqueous dispersion of this Example gave a glossmeter reading of 7 for the coating of seven coats having a total thickness of 10.1 microns.

#### EXAMPLE 3

The procedure of Example 1 was repeated except that the copolymer of the copolymer (b) aqueous dispersion was tetrafluoroethylene/perfluoro(propyl vinyl ether) copolymer having an infrared ratio of 2.80 ( $A_{10.07\mu}/A_{42.25\mu}$ ) and a specific melt viscosity of about  $140 \times 10^4$  poises at  $380^\circ\text{C}$ . at a shear stress of 6.5 psi. The dispersion of this copolymer was 60 percent polymer base solids based on the weight of the dispersion and contained 6 percent "Triton" X-100 based on the weight of the copolymer (no extra "Triton" X-100 was added to the co-dispersion). The composition comprising tetrafluoroethylene polymer (a) aqueous dispersion, copolymer (b) aqueous dispersion, and nonionic surfactant in the proportions set forth in Example 1 except as otherwise indicated herein gave a glossmeter reading of 12 on the coating comprised of 7 coats of a total thickness of 9.2 microns, as compared to a glossmeter reading of 6 for the coating prepared from polytetrafluoroethylene aqueous dispersion by itself.

#### EXAMPLE 4

The procedure of Example 1 was repeated except that the surfactant was a mixture of



and



wherein x, y and z are 10—11, 12—13, and 4—5, respectively, available as "Alfonic" 1012—60 and DN—65, respectively, the former being present in the amount 1.8 per-

cent and the latter 7.3 percent (by weight), based on the total weight of polymer solids (60 percent by weight) in the polytetrafluoroethylene dispersion. The codispersion-surfactant composition (no extra surfactant added to co-dispersion) gave a glossmeter reading of 17 for the coating comprising seven coats having a total thickness of 9.6 microns, as compared to a glossmeter reading of 6 for coating prepared from the polytetrafluoroethylene aqueous dispersion alone. The average particle diameter of the polytetrafluoroethylene in this Example was 0.34 micron.

The terms "TRITON" and "ALFONIC" as used in this specification are Registered Trade Marks.

10 WHAT WE CLAIM IS:—

1. A coating composition which comprises an aqueous dispersion of:  
(a) a non-melt-fabricable (as hereinbefore defined) tetrafluoroethylene polymer,  
(b) 1 to 6% by weight, based on the weight of (a), of a melt-fabricable (as hereinbefore defined) tetrafluoroethylene copolymer, and containing, dissolved therein, a non-ionic surfactant.

2. A composition according to claim 1 wherein the tetrafluoroethylene polymer (a) has an average particle diameter of at least 0.3 micron.

3. A composition according to claim 1 or 2 wherein the proportion of solids of tetrafluoroethylene polymer (a) and copolymer (b) is from 40 to 65% by weight, based on the total weight of the composition.

4. A composition according to any one of claims 1 to 3 wherein the proportion of nonionic surfactant is from 4 to 9% by weight, based on the total weight of the composition.

5. A coating composition according to claim 1 substantially as hereinbefore described.

6. A process for forming a coating on a substrate which comprises applying to the substrate a composition as claimed in any one of claims 1 to 5, drying the composition and sintering the tetrafluoroethylene polymer (a).

7. A process for forming a coating on a substrate according to claim 6 substantially as hereinbefore described.

8. Coated articles whenever prepared by a process as claimed in claim 6 or 7.

9. A process for preparing a film which comprises coating a smooth surfaced substrate by a process claimed in claim 6 or 7 and then removing the coating.

10. A process according to claim 9 substantially as hereinbefore described.

11. Film whenever prepared by a process as claimed in claim 9 or 10.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1973.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.